NRL Report 6329

Factors Affecting the Icing Resistance of Lubricants for Aircraft Ordnance

H. R. Baker and R. N. Bolster

Surface Chemistry Branch
Chemistry Division

October 21, 1965

U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Copies available from Clearinghouse for Federal Scientific and Technical Information (CFSTI, Sills Building, 5285 Port Royal Road, Springfield, Virginia 22151
$2.00

ABSTRACT

Recent samples of the all-weather semifluid lubricant for aircraft ordnance, both from manufacturers and from Navy stocks, have failed to meet the cold-sweat-cold gun firing test required by Military Specification MIL-L-19701 (NOrd). These failures were due to ice adhesion attendant on the poor water resistance of the lubricants. The probable cause of the loss in water resistance was the presence in the lithium stearate thickener of surface-active impurities such as sodium soaps and soaps of myristic and oleic acids. These impurities can be detected by measurements of surface tension lowering. It is probable that the water resistance of other lithium stearate thickened greases are also affected by these impurities. The investigation established that variations in raw materials other than the soap were not major contributors to the difficulties encountered.

A lubricant of altered formulation has been developed and shown to be superior to the original lubricant. Variations in the consistency of the improved lubricant over a wide temperature range were found to be much less than those of the original lubricant. Resistance to water and to ice adhesion are increased. This material has successfully lubricated the Mk 12 machine gun equipped with the Mk 7 pneumatic feeder under ambient temperature and cold-sweat-cold conditions. This formulation retains all of the useful properties of the original lubricant, such as compatibility with MIL-P-5516 oil-resistant rubber, resistance to evaporation loss, corrosion inhibition, and antiwear protection.

Several new testing procedures have been developed and evaluated, and existing tests have been re-examined. No reliable substitute for the gun firing test has been found, but screening tests for evaluating separately some of the lubricant's qualities have been developed and norms established for greases known to be successful in the gun firing tests.

PROBLEM STATUS

This is a final report on this phase of the project. Work on other phases of the project is continuing.

AUTHORIZATION

NRL Problems C02-04 and C02-12
BUWEPS Project RRMA03-021/652-1/R001-07-01-17-3
ONR Project RR 001-01-43-4752

Manuscript submitted July 26, 1965.

FACTORS AFFECTING THE ICING RESISTANCE OF LUBRICANTS FOR AIRCRAFT ORDNANCE

INTRODUCTION

An earlier report from this Laboratory (1) described the development of a semifluid lubricant suitable for use on the 20-mm Mk 12 machine gun carried on some naval aircraft. A specification, MIL-L-19701 (NOrd) (2), was issued, a supplier qualified, and grease has been purchased under the specification for the past eight years. Recent failures of the lubricant in qualification tests and the failure of other potential suppliers to pass the tests have required a re-examination of this grease formulation and its performance.

The major problem in the development of the MIL-L-19701 lubricant had been formulation to secure resistance to icing during the cold-sweat-cold cycling tests at -65 F. The low-temperature firing tests are expensive, and there was insufficient firing experience to provide a reliable correlation between these tests and the bench test of icing resistance described in the report. Consequently, a composition was specified for the lubricant, together with laboratory tests of consistency, oxidation stability, and rubber compatibility. A cold-sweat-cold firing test of four satisfactory cycles to -65 F was required for qualification of a product, but not for acceptance of later lots of the same composition from the same manufacturer. It was expected that under these conditions later procurements could be depended upon to have the same icing resistance as the qualifying lot, and in fact no reports of icing difficulties in the presence of this lubricant have been reported from the fleet. It is believed, however, that lubrication in the field has been required more frequently than is desirable.

It was pointed out in Ref. 1 that the final phases of the investigation (completed after the program of firing tests on the experimental lubricant GLT-700-60 had been accomplished) indicated that further improvements in the formulation were possible. However, the GLT-700-60 had passed seven cycles of cold-sweat-cold firing; it appeared adequate for the purpose intended, and firing tests on proposed improved versions of the lubricant would have cost ten or fifteen thousand dollars. It was concluded that the expense was not justified, and the specification was established on the basis of the field experience with the material already developed. GLT-700-60 had been formulated from material procured eight to ten years earlier by this Laboratory in connection with another problem; the lithium stearate was a specially selected lot of a type no longer commercially available and the phenylstearic acid was a pilot lot supplied by an oil company which was no longer interested in its commercial production. The supplier for MIL-L-19701 made every effort to procure high-quality materials for his qualification lot, and this Laboratory found the materials used to be of excellent quality. The lubricant submitted passed four but not five cycles on the cold-sweat-cold test (as compared with seven for the original NRL product). The difference was attributed to problems in scale-up of the grease gelling and dispersing procedure, and the lubricant was qualified under the specification.

Because of the Government's policy of procurement by competitive bidding, two other potential suppliers were urged to submit products for qualification, and they complied. The products offered conformed to the composition called out in the specification and met the laboratory tests approximately. Both products, however, failed to pass the four cycles of the cold-sweat-cold firing tests at the U.S. Naval Weapons Laboratory at Dahlgren, Virginia. A question was raised as to whether the firing tests were being conducted in exactly the same manner as those performed several years earlier by different

personnel with different guns. Firing tests were then conducted with a sample of MIL-L-19701 lubricant from current naval stocks, which also failed to pass the required number of cycles

A conference was held at the U.S. Naval Research Laboratory on September 21, 1961, at which four possible causes were suggested for the failure of all samples to pass the low-temperature firing tests, as follows:

1. The specific guns used in the earlier tests were not available; the guns used recently may have been modified in minor points of design or finish in such a way as to increase susceptibility to ice interference.

2. The personnel who supervised the earlier tests were no longer at Dahlgren. Thus minor details of the cold-sweat-cold procedure may have been modified in such a way as to increase the severity of the recent tests.

3. The raw materials presently used in formulation of the lubricant may have contained different kinds or amounts of impurities than were present in the materials used for the development and original qualification of the lubricant.

4. The methods of manufacture used for the recent samples may have differed from those originally used in such a way as to give a less favorable colloid structure to the lubricant.

It was agreed that representatives of NRL familiar with the original firing tests would visit the U.S. Naval Weapons Laboratory to discuss test procedures, examine the guns used for the present tests, and witness lubricant behavior during tests. It was agreed that NRL would examine samples of the raw materials utilized in producing current samples of lubricant, and investigate the effect of impurities and formulation techniques on lubricant characteristics. It was also agreed that NRL personnel would attempt to devise laboratory tests of icing resistance that would give reliable correlation with low-temperature firing tests.

In connection with the new firing tests observed by NRL, some minor modifications were made in the handling of the guns during the firing cycles; but these changes did not produce a significant increase in lubricant performance. It was also noted that the guns used in the recent tests differed from those employed in 1954 and earlier in that they lacked relief grooves on some sliding surfaces in the breechblock mechanism. Further firing tests using the earlier style of grooved slides in the present weapon showed an increase of about one cold-sweat-cold cycle before failure in the low-temperature firing test. The improved performance still failed to meet the specification.

Observations of sweating and icing behavior showed that condensation deposited upon removal from the cold chamber was washing off a much larger proportion of the lubricant than had been noted in the earlier tests. Examination of the guns after freezing showed ice to be present between plane bearings in continuous thin sheets. Such sheets had not been a prominent feature of the earlier tests. It was concluded that, while the guns and cycling procedures of the 1961 tests probably provided a more severe test than the guns and cycling procedure used in the original qualification, such changes were not the major cause of the poorer firing performance in the recent tests. As a result of these supplementary firing tests it was agreed that laboratory studies directed toward the following objectives would be undertaken at the U.S. Naval Research Laboratory:

1. The development of significant screening tests which could be correlated with the gun firing test data

2. Examination of the effect of variations in raw material purity and in manufacturing procedures on the characteristics of the lubricant, with special attention given to washing resistance and bench icing tests

3. Study of the effects of formulation and/or manufacturing variables on the performance of the lubricant in screening tests and eventually in firing tests (for the most promising variations).

The results of such studies are presented in this report.

RESULTS

Investigation of Failures of the MIL-L-19701 Lubricants

Acting under the assumption that changes in the raw materials were causing deficiencies in the lubricant performance, the investigation was initiated by preparing laboratory batches of the lubricant in which the raw materials supplied by the various producers were systematically compared. Unfortunately, the retained samples of the original lubricant had deteriorated during ten years of storage and could not be relied upon for comparisons, so the laboratory formulations could be compared only with each other and with the recently produced commercial samples. Three of these samples which had been gun tested were examined in the laboratory. Two of these samples were from prospective suppliers, submitted for gun testing for qualification (3); one was of a lubricant in production (4). These three lubricants will be referred to in this report as lubricants A, B, and C. The formulation of the lubricants is shown in Table 1.

Table 1
Specified Formulation for MIL-L-19701 Lubricant (2)

Component	Weight-%
Isodecyl pelargonate	29.5
Bis(2-ethylhexyl) sebacate	9.0
Dimethyl silicone fluid, 7 cs	40.3
Slightly phenylated silicone fluid, 50 cs	14.5
4-tert-butyl-2-phenylphenol	0.4
Phenylstearic acid	2.6
Lithium stearate	3.5

±1% to produce desired consistency.

An examination of the lithium stearate samples furnished by the producers of the three greases which had been subjected to gun firing tests revealed that their content of acetone-soluble material (largely fatty acids) varied between 0.6 and 1.0%. Previous experience at this Laboratory has shown that acetone solubles in excess of 0.5% might affect the consistency of greases. Two series of greases were therefore prepared in which the only variable was the source or treatment of the lithium stearate. The lithium stearates were used both as received from the grease formulator and after extracting with acetone and drying. The greases containing lithium stearate which had been washed with

acetone and dried were of slightly higher apparent viscosity but showed no appreciable differences in cold-sweat-cold (c-s-c) piston and cylinder tests and in continuous condensation tests.* The consistency decrease caused by the excess free fatty acids could be compensated by increasing the amount of lithium stearate used.

It was concluded that the acetone-soluble materials in the lithium stearate were not related to any of the variations observed between lubricants A, B, and C and were not responsible for the much larger differences in low-temperature firing performance between these lubricants and that originally developed at this Laboratory. (Further investigation of lithium stearate purity, discussed later in this report, has revealed other factors which are related to this difference in performance.)

The phenylstearic acids used in the preparation of recent lots of the gun lubricant were procured from different sources than the acid used in the original development of the lubricant; those from the new source were of higher purity than the original acid, which was no longer available. Lubricant formulations in which the phenylstearic acids supplied by the three commercial producers were the only variable showed no difference in performance patterns. The phenylstearic acids submitted by the three suppliers must be considered substantially equivalent.

Greases made up without phenylstearic acid were very resistant to water in the continuous condensation test and gave very low torques and long life in the cold-sweat-cold piston and cylinder test, but they had poor rust resistance. The use of less than 2.8% of phenylstearic acid gave lubricants intermediate in properties between the acid-containing and the acid-free formulations.

The effects of the oxidation inhibitor 4-tert-butyl-2-phenylphenol and of samples of phenyl-α-naphthylamine furnished by each of the suppliers were compared in lubricant formulations identical except for the oxidation inhibitor used. The resulting greases were indistinguishable in various cold-sweat-cold and water resistance tests.

When each of the four oil components (Table 1) was examined as an independent variable by formulating lubricants differing only in the commercial source of one oil, no significant differences were found between the formulations. It was concluded that impurities in the current supplies of the base oils were not responsible for the poorer low-temperature gun test performance of the lubricants A, B, and C.

Development of an Improved Formulation

Since no sufficient reason for the failures of recent lubricants had been found in studies of their constituents, attention was turned to improving the formulation and method of manufacture. In a previous report (1), this Laboratory indicated the probability that the formulation recommended at that time could be improved by modification to include a sulfonate rust inhibitor if circumstances ever justified the expense of another series of low-temperature firing tests. During the present study, formulations containing sodium dinonylnaphthalene sulfonate (NaDNNS), ethylenediamine DNNS, barium DNNS, and basic barium DNNS were examined, and those containing barium sulfonates were found to give outstanding performance in the laboratory screening tests. This improvement results from the reduction in the amount of phenylstearic acid present. As was noted in the discussion of phenylstearic acid source and purity, greases made without this additive were superior in water resistance but lacking in rust inhibition. Substitution of barium sulfonate inhibitors for part of the phenylstearic acid simultaneously improved the water resistance and the rust inhibition of the grease and reduced its corrosive

*Experimental techniques for these tests are described in Appendix A.

action on brass and copper. The phenylstearic acid was not eliminated entirely, because of its value as an oiliness additive. Also, it has been found more effective than the BaDNNS additive in reducing the adhesion of ice to lubricated surfaces (5). The composition of the improved lubricant, which will be referred to as composition D, is shown in Table 2.

Table 2
Formulation of Improved Lubricant D

Component	Weight-%
Isodecyl pelargonate	28.6
Bis(2-ethylhexyl) sebacate	9.0
Dimethyl silicone fluid, 7 cs	39.2
Slightly phenylated silicone fluid, 50 cs	14.2
4-tert-butyl-2-phenylphenol	0.4
Phenylstearic acid	1.0
Basic barium dinonylnaphthalene sulfonate solution (50% in volatile solvent)	2.0
Lithium stearate	5.6*

*±1% to produce desired consistency.

In the past, most of the semifluid lubricants were prepared by incorporating the lithium stearate into a vehicle consisting mainly of the esters and the oxidation inhibitor. After chilling and milling, this lithium grease concentrate was blended on the mill with the silicones and the rust inhibitor. Such a procedure permitted solution of the soap at a lower temperature and gave a higher final consistency than if the rust inhibitor was present in the mixture during initial chilling and formation of soap structure. During the present study, lubricants prepared by this blending procedure have been critically compared with lubricants prepared by including all of the components in the original melt, so that no cut-back or blending step was involved. (Some changes in soap content and final milling schedule were required with the single-step procedure.) When lubricants of the same final consistency were compared, it was found that the one-step process gave a product having a lower tendency for oil separation, better adhesion to metal surfaces, and higher water resistance than lubricants prepared by the two-step procedure involving cut-back of a soap concentrate. This improvement is believed to result from more uniform distribution of the soap phase in the one-step process. When the soap structure is formed in the ester and the concentrate diluted with silicone, the small clusters of soap crystallites remaining after milling tend to retain an ester-rich phase while the intercluster liquid remains richer insilicone. Flocculation of the soap crystallite clusters tends to reduce the total volume inhabited by soap aggregates, resulting in syneresis of the interparticle oil.

The increased mechanical stability of the one-step grease may result in part from the fact that the percent of lithium stearate required is 50 to 100% greater than for a two-step-blended lubricant of equivalent consistency. The increased soap content required in one-step greases is a direct result of the presence of the rust inhibitor during soap crystallization. The readily adsorbed inhibitor either changes the crystal habit of

the soap so that the surface-to-volume ratio of the crystallites is reduced, or it blocks off polar sites for the particle-particle interactions that are responsible for the re-establishment of structure after shear (thixotropy). The rust inhibitor also reduces the rate at which the soap structure approaches its equilibrium state. This is particularly noticeable when barium DNNS or basic barium DNNS is present. After the initial chilling and milling, such formulations have low or soupy consistencies; but on storage at 50 C for 8 to 32 hours, the consistency rises to a value suitable for gun lubrication. Experience with such low initial consistencies had discouraged earlier attempts to use petroleum sulfonates as rust inhibitors in MIL-L-19071 lubricants.

Lubricant samples A, B, and C contained undispersed (unmelted) lithium soap particles. These were readily seen when a film of the grease was mounted on a glass slide and examined by transmitted light at 100x magnification. In bench-scale preparations the persistence of such unmelted particles could be prevented if the soap was well dispersed in the oil and if the dispersion was heated to a sufficiently high temperature for complete solution. When the oil phase consisted of esters alone, 185 C was an adequate temperature. The presence of silicones raised the solution temperature, so that it was 200 C when 60% of the oil phase was silicone.

The procedure used in the preparation of laboratory samples of the improved lubricant is given in Appendix A. It is realized that small-grade laboratory procedures for the production of greaselike lubricants are not directly comparable with the operations involved in commercial preparation of the same lubricant. We believe, however, that laboratory experience will be helpful in devising the large-scale procedures, so these observations and those in Appendix A are reported for whatever value they may have to commercial suppliers.

The improved lubricant was found to have an unusual and advantageous apparent viscosity-temperature relationship as shown in Fig. 1. Above 120 F and below 30 F, grease D shows normal behavior, becoming increasingly viscous as the temperature decreases. Between 120 and 30 F, however, the viscosity decreases with falling temperature so that this grease has a nearly uniform consistency over a wide temperature range. Grease C shows a similar but much smaller inverse behavior in the higher temperature region. The cold-sweat-cold piston and cylinder and cold-sweat-cold washing resistance tests have shown that high apparent viscosity at room temperature helps to improve the water resistance of the lubricant, while the cold-sweat-cold gun firing test has shown that low apparent viscosity at low temperature is helpful in preventing slides-out-of-battery failures. The consistency-temperature properties of the improved formulation help to reconcile these opposing requirements.

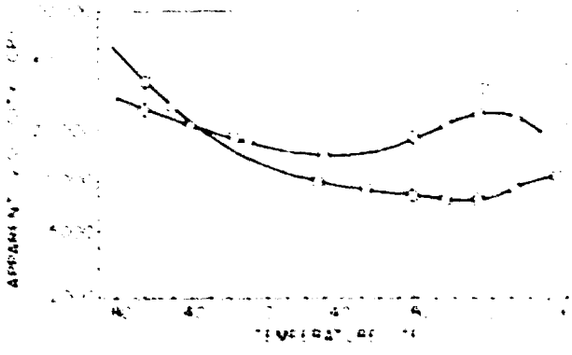


Fig. 1 - The effect of temperature on the consistencies of a MIL-L-19701 formula grease, C, and a grease of the improved formulation D, as measured by a Brookfield viscometer at 12 rpm

The rheology of the improved lubricant at room temperature is complex. The material has a yield point, and the apparent viscosity decreases as the shearing rate increases in the range investigated. Dilatancy was observed at some shearing rates with greases having unusually coarse structure. Thixotropy was normally low, and the greases were quite work stable.

As was mentioned in the discussion of preparation procedures, this grease has a very low consistency

when first made. As it ages, the consistency rises into a useful range. The rate of this process is controlled by the storage temperature, being more rapid at higher temperatures. With most laboratory samples the consistency was not stable but decreased after the maximum, approximately in inverse proportion to the logarithm of the time elapsed. The apparent viscosity at -65 F increased more than that at 77 F, reducing the favorable consistency-temperature characteristic of the lubricant. Cold-sweat-cold piston and cylinder test performance also declined with age. Commercially prepared samples have subsequently shown much less consistency loss with age; thus this loss is not expected to be a serious problem in production, although some decline in the cold-sweat-cold piston and cylinder test performance has been observed. The change in the consistency-temperature characteristics can be followed by plotting apparent viscosity at -65 F against that at 77 F as the lubricant ages. Shown in Fig. 2 are typical curves for a MIL-L-19701 formulation grease and a laboratory sample of the improved formation. The diagonal broken line indicates equal consistencies at both temperatures. It can be seen that the MIL-L-19701 grease is farther from this desirable region than the improved grease, and that the improved grease loses some of its advantage as it ages. Most of the commercially prepared samples of the improved grease do not follow the decline in consistency shown for this laboratory sample.

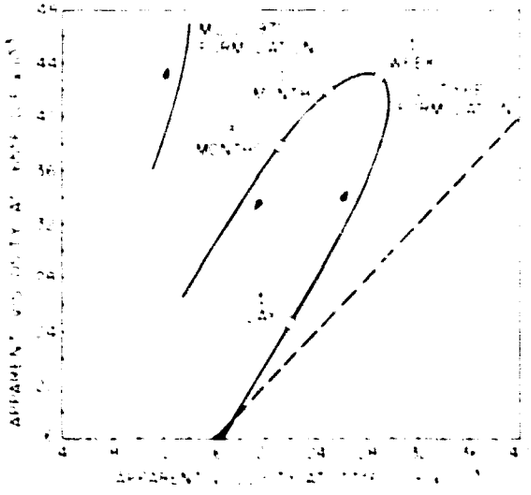


Fig. 2 - Comparison of consistency-temperature properties and their changes with age

In addition to formulation D shown in Table 2, two other promising formulations were evaluated. Formulation E was similar to D, but the basic BaDNNS was replaced with neutral BaDNNS. Formulation F was similar to D except that the 7-cs silicone was eliminated, being replaced by an increase in the percent of 50-cs slightly phenylated silicone. This substitution raised the 100 F viscosity of the base oil from 8 to 14.6 cs, and the -65 F viscosity from 320 to 1300 cs. It was expected that such a viscosity increase would improve the performance of the lubricant in heavily loaded configurations at ambient and higher temperatures. This would be desirable if the lubricant still gave satisfactory performance at -65 F.

On the basis of laboratory test results, it was recommended that greases D, E, and F be subjected to gun firing tests. The results of the laboratory and gun firing tests (6) of these lubricants are given in Table 3, along with the data for lubricants A, B, and C of the MIL-L-19701 formulation.

The lubricant formulation D, containing the basic BaDNNS, passed the gun test as expected. In the cold-sweat-cold piston and cylinder test, it had passed several more cycles before failure than the MIL-L-19701 greases. The coalescing activity in the sustained condensation test was much greater, and the consistencies at -65 F and 77 F were both improved. Rust inhibition, as shown by the water drop washing resistance test, was also improved. Lubricant E, containing the neutral BaDNNS, provided an enormous increase in rust inhibition, but its cold-sweat-cold piston and cylinder and condensation test performance was poorer, and it did not pass the gun firing test. Lubricant F, containing 50-cs slightly phenylated silicone in place of the 7-cs dimethyl silicone, was much poorer in the gun test than was expected from the cold-sweat-cold piston and cylinder test, but the gun test result was consistent with the result of the sustained condensation

Table 3
Lubricant Test Results, Lubricants A, B, C, D, E, F

Test	F	B	C	A	E	D
C-s-c gun firing (av. cycles passed)	1	1.5	2	2.5	2.5	4.5
C-s-c gun firing (av. cycle of first slides-out-of-battery failure)	2	≥2.5	≥3	≥3.5	3.5	≥5.5
C-s-c gun firing (av. cycle of first frozen bolt failure)	2.5	2.5	3	3.5	4	≥5.5
C-s-c piston and cylinder (cycles to failure)	8	7	6	6	9	10
Sustained condensation (rate of coalescence)	very slow	slow	slow	moderate	moderate	rapid
Water-drop washing resistance (vol. of sol'n* to rust, ml)	56	32	31	34	>312	58
Apparent viscosity at 77°F (cp)†	21,000	7500	9000	6500	11,000	11,000
Apparent viscosity at -65°F (cp)†	31,000	32,000	38,000	31,000	32,000	21,500

*3% sodium chloride.
†Using Brookfield viscometer at 12 rpm.

test. The failure was traced to the fact that mixing water with the grease caused complete separation of the oil and soap phases. None of the greases using the four-oil blend as given in Tables 1 and 2 separated, nor did samples containing only dimethyl silicone fluids with the esters, nor those containing only ester oils.

Four-ball wear tests were made on the oil and additive blends used in lubricants D, E, and F to ensure that the lubricity of the grease was not reduced by the change in rust inhibitor. The wear scars were found to be smaller than with the previous oil blend and comparable to those found with a pure diester oil (0.65 mm for oil blend D)

The lubricant formulation D containing basic BaDNNS was thus found to offer several improvements over the previous lubricant, while retaining its useful properties. It provides (a) control of rubber swell, (b) protection against the adverse effects of evaporation of the oils during high-temperature exposure, (c) improved corrosion inhibition, (d) good antiwear properties, (e) resistance to water wash-off and ice adhesion, and (f) greatly improved low-temperature consistency.

The Effect of Water-Sensitive Impurities in Lithium Soaps on Lubricant Properties and Performance

The qualification samples (G, H, and I, Table 4) made by the three suppliers according to the improved formulation were disappointing. The data of Table 4 show that although the cold-sweat-cold piston and cylinder tests for some samples were promising the cold-sweat-cold gun test performance was little improved. Different modes of failure were encountered in the gun tests, and a critical examination revealed a relationship between the modes of failure and other properties of the lubricants.

Table 4
Lubricant Test Results, Lubricants G, H, I, and J

Test	G	H	I	J
C-s-c gun firing (av. cycles passed)	1	1	2	2
C-s-c gun firing (av. cycle of first slides-out-of-battery failure)	-	2	3	3
C-s-c gun firing (av. cycle of first frozen bolt failure)	2	≈3.5	≈3.5	≈4
C-s-c piston and cylinder (cycles to failure)	8	11	13	11
Apparent viscosity at 77°F (cp*)	36,000	16,000	30,000	19,000
Apparent viscosity at -65°F (cp*)	60,000	34,000	51,000	25,000
Frost and condensation (av. score)	0.5	1.9	2.5	1.8

*Using Brockfield viscometer at 12 rpm.

Samples A, B, C, and G had failed through immobilization of the gun mechanism due to ice adhesion (frozen bolt). These lubricants were also poorest in cold-sweat-cold piston and cylinder test performance. Samples E, F, H, and I, on the other hand, failed because stiffening of the lubricant at low temperatures made the guns sluggish in operation. The movement of the breechblock slides into battery position is accomplished by inertia and coil-spring energy. The low driving force and large bearing area make this mechanism sensitive to lubricant stiffness, resulting in slides-out-of-battery failure. The average cycles in which these types of failure were first encountered are also given in Tables 3 and 4.

There appeared to be some correlation between the low-temperature apparent viscosities of the lubricants and the cycles in which slides-out-of-battery failures first occurred, which indicated that the previously recommended consistency had been too high. The recommended maximum consistency of the grease was therefore reduced and the supplier of the most promising sample, I, was asked to supply sample J of identical composition except for the thickener content. As is shown in Table 4, no improvement was found in laboratory or gun firing test performance. It became apparent that the sluggishness of operation which caused failure resulted not from the small differences in the low-temperature lubricant viscosities but from a much more serious stiffening of the lubricant by finely divided ice crystals formed by freezing of the water which had been emulsified in the oil during the sweating phase. It was also apparent that the greases E, F, G, H, and J were much less resistant to this emulsification than the prototype D.

To study the sweating process and the resulting emulsification more fully, the frost and condensation test was developed. In this test frost is allowed to form on a chilled metal surface, and the lubricant behavior is observed during melting. The lubricants were scored between zero and five on their water resistance as evinced by the rate of coalescence and shapes of the water droplets. Higher scores implied better performance. The results for samples G, H, I, and J are shown in Table 4. The low score of sample J as compared to I explained why no improvement was realized from the decrease in consistency. All of the scores were poorer than that of the successful sample D. which had a score of 3.2. Although variations in the preparation of the samples were

a conceivable cause of the increased tendency to emulsify water, the presence of surface-active impurities in the lubricant components appeared to be a much more likely cause.

Samples of the components used in lubricant sample J were obtained from the lubricant producer. These materials and greases made using them were compared with materials previously used and earlier grease preparations. The cold-sweat-cold piston and cylinder test and the frost and condensation test were used in comparing the grease samples.

The ester oils were examined for volatile impurities and hydrolysis products by determining their closed-cup flash points. They were examined for water-soluble and surface-active impurities by observing the spreading tendencies of drops on water. Differences were found between oils from various sources, but these variations were small and resulted in no significant differences in greases made from them. Purification of the ester and silicone oils by distillation also made no difference in the grease.

The effect of the source of the lithium stearate was then examined, and the recent soap sample was found to be the defective component. When it was replaced by soap of the lots used for earlier greases, the test performance improved greatly. Purification of the soap by washing with acetone and benzene to remove free fatty acids had no effect on the performance of the grease, as was found in the earlier investigation of the MIL-L-19701 lubricant materials. Washing the soap with water, however, did improve the performance of the grease, showing that the surface-active impurities were soluble or dispersable in water.

This observation provided a useful method for measuring the surface-active impurity content of the soap samples by determining the surface tension lowering produced in water infusions of the sample. A number of lithium stearate samples on hand were tested in this manner, and test data were collected on all of the grease samples that had been prepared from these thickeners. Table 5 shows that there is a good correlation between the performance of the greases in the frost and condensation and cold-sweat-cold piston and cylinder tests and the surface tensions of the thickener infusions. The thickeners are listed in the order of these surface tensions. The correlation with the available gun firing test results was similar. Thickener 7 was used in grease J which failed in the gun test; thickener 3 was used in grease D, which passed. The surface tension measurement is a quick and simple method of determining whether a thickener is pure enough for use in the grease, 27 dynes/cm being the lowest value encountered that gave an acceptable laboratory grease. Although this test cannot be applied to the finished grease as an acceptance test, it should be useful in checking the quality of the thickener before manufacture of the grease.

There were two likely sources of surface-active impurities in the lithium stearate: (a) sodium or potassium soaps, and (b) soaps of acids other than the stearic and palmitic normally present. Analyses of the thickener samples showed sodium to be present in small amounts in some and in large amount in the poorest (7, Table 5). Sodium and potassium soaps are much more water soluble than the corresponding lithium soaps and are therefore more surface active. Similarly, myristate and oleate soaps are more water soluble and more likely to adsorb at the oil water interface than the longer chain, saturated soaps. The thickener samples were hydrolyzed and the fatty acids analyzed for oleic acid by iodine value determination, and for stearic, palmitic, oleic, and myristic acids by chromatography. As is shown in Table 5, variations in the oleic and myristic acid contents were found. It can be seen from these data that large amounts of lithium myristate or oleate are harmful (thickeners 4, 5, and 6). Sodium myristate and oleate, because of their greater water solubility, are even more harmful (thickeners 7 and 8). This was confirmed by analyses of the solids from evaporation of the infusion of thickener 7. Sodium was present in greater amounts than lithium, and the extracted acids were largely myristic and oleic. Small amounts of sodium stearate or palmitate in the

Table 5
Lithium Stearate Characteristics

Lithium Soap Sample*	Surface Tension of Infusion (dynes/cm)	C-s-c Piston and Cyl. Test (cycles)	Frost and Cond. Test Score	Oleic Acid (%)	Myristic Acid (%)	Sodium Spectrum Strength
9	41.1	17	3.8	-	-	weak
1	40.9	16	3.7	2	1.6	very weak
2	28.3	15	3.3	6	1.6	none
3	27.3	15	3.1	6	2.2	none
4	26.4	15	3.0	8	-	none
8	26.3	12.5	2.8	7	-	medium
5	26.3	18	2.4	15	2	none
6	24.5	15	2.4	5	12	none
7	23.4	10	2.36	7.5	1.5	strong

*1 and 4 - Supplied by a lubricant manufacturer
2 - Purchased by NRL
3 - Supplied by a lubricant manufacturer, used in grease D
5 - 90% 3 + 10% lithium oleate
6 - 90% 3 + 10% lithium myristate
7 - Supplied by a lubricant manufacturer, used in grease J
8 - 7, water washed
9 - Retained sample, used in original NRL grease.

thickener are not harmful in the absence of the myristate and oleate (thickener 1). Small amounts of lithium myristate and oleate are not harmful in the absence of sodium (thickeners 2 and 3).

For minimum acceptable performance, it is recommended that the soap used as a thickener be sufficiently pure to yield surface tension values of 32 dynes cm or greater. This can be achieved with an all-lithium soap made from a stearic acid containing less than 2% myristic and 4% oleic acids.

For maximum lubricant performance, the use of a purer lithium stearate, similar to number 1 in Table 5, is recommended. Such a material will give an infusion surface tension of 40 dynes cm or more. The use of this thickener in laboratory preparations improved the water resistance of the grease considerably. Such lithium stearates would be made from a purer stearic acid, such as the "triple pressed" grade rather than the "double pressed" usually employed for grease making. Sodium and potassium content should be as low as possible. Such a material can be produced commercially. It has been observed that lubricant samples prepared by large-scale commercial processes are usually inferior to those prepared in the laboratory using materials of comparable quality. It is therefore important that commercial producers obtain the best materials available to offset this disadvantage.

It is probable that the earlier failure of the MIL-L-19701 lubricants to pass the low-temperature firing test was due to the presence of surface-active impurities in the thickeners. A retained sample of the thickener used during the original developmental work was also examined (9, Table 5). Although some sodium was detected with the flame test, the surface tension of the soap infusion was much higher than that of most of the soaps used in the current work, and comparable to the best one examined. The use of such a thickener in the MIL-L-19701 formulation might well restore its performance capability in the gun firing test. In the improved formulation, it provides still better performance.

The use of a pure lithium stearate is required in this gun lubricant because its consistency makes it more susceptible to water emulsification than stiffer greases and because the conditions to which it is exposed are unusually severe. However, many other greases required to be water resistant, such as automotive chassis grease, might be improved significantly at small cost by using a purer lithium stearate in their manufacture.

To establish the validity of the conclusions reached in this investigation, cold-sweat-cold gun firing tests were conducted with lubricants manufactured in accordance with the recommendations of this report. Two lubricant samples (designated K and L) were prepared at NRL by the technique described in Appendix A. The oil blends of the two samples were identical and were formulated in accordance with Table 2, except that 2,6-di-tert-butyl-4-methylphenol was used as the oxidation inhibitor. The oils were of commercial grade and were not purified. The lithium stearate used in lubricant K was from a retained sample of soap used in the original developmental work (number 9, Table 5). The lithium stearate used in lubricant L was prepared by a commercial supplier in response to a request for a soap low in oleates, myristates, and sodium. The infusion surface tension technique showed this material to contain less surface-active material than any other thus far examined (Tables 5 and 6). The amounts of thickener required in Lubricants K and L were 6.3 and 5.3%, respectively.

The results of laboratory tests of these lubricants are given in Table 6. These results were satisfactory except for the low-temperature consistency of lubricant K after accelerated aging. These tests were performed in accordance with the methods described in the recommended technical requirements for revision of the specification (Appendix B).

Cold-sweat-cold gun firing tests of these two samples were conducted by the U.S. Naval Weapons Laboratory. The results are given in Table 6. With lubricant K, one gun failed on the fifth cycle, as a result of excessive resistance to operation of the charging mechanism. The other gun was still charging easily and firing at a high rate when the test was discontinued after seven cycles. With lubricant L, no difficulties were encountered. This performance exceeds that attained in the development of the original lubricant (1), in that the firing rates were higher. The resistance of both lubricants K and L to emulsification and wash-off was excellent. Very little oil was present in the condensate dripping from the guns during the sweating phase, and ice-grease mixtures scraped from the guns after firing were observed to separate readily upon thawing.

Because resistance to water emulsification is so important to the performance of the lubricant, another attempt was made to develop a water resistance test suitable for application to the finished lubricant. This led to the emulsification resistance test, in which the solvent-diluted lubricant was emulsified with water and the rate at which water separated from the emulsion was observed. The results of this test of lubricants K and L is given in Table 6. Lubricants made from less pure lithium stearate separated much more slowly. For example, with lubricant G no separation occurred after standing for several days.

Table 6
Lubricant Test* Results, Lubricants K and L

Test		K	L
Lithium Stearate Purity			
Surface tension of aqueous lithium stearate infusion (dynes/cm)		41.1	45.7
Consistency (cp)			
"As received"	77°F	22.125	24,000
	-65°F	34,000	22,500
After 168 hr at 77°F	77°F	19,750	22,000
	-65°F	35,500	23,000
After 168 hr at 120°F	77°F	23,125	26,625
	-65°F	45,125	32,750
Work stability		112°C	107°C
Icing Resistance (Cold-sweat-cold piston and cylinder test)			
Satisfactory cycles		39 39	41 41
Emulsification Resistance			
Time to separation of 5 ml water		25 min	1 min
Cold-Sweat-Cold Gun Firing			
Satisfactory cycles	1st gun	7	5
	2nd gun	4	7

*Test methods as described in Appendix B.

Summary of Test Method Characteristics

One of the tasks assigned the U.S. Naval Research Laboratory was to improve the gun lubricant testing procedures by developing new tests and by examining existing tests more thoroughly. Many possible tests were considered during this study. Some of these have proven useful in studying various lubricant properties; others have not. Unfortunately, no single test has been found capable of replacing the cold-sweat-cold gun firing test because of the numerous variables simultaneously influencing the results in this test.

The details of the testing procedures are described in Appendix A. Some observations of experimental phenomena encountered and some comments on the significance of the tests follow.

Gun Firing Tests – The ambient-temperature firing tests using unmodified guns were completed successfully with all lubricants studied. It was in the cold-sweat-cold testing that failures occurred. This test is still the best simulated service test available,

although it may be more severe than most service conditions. Although flight test results may be more representative of service performance, the lack of control over temperature, humidity, and other conditions reduces the reliability of such tests.

Two types of lubrication failures were encountered. The first type was characterized by failure of the breechblock to move when the charging mechanism was energized. The breechblock slides usually moved slightly, but not enough to unlock the breechblock. This type of failure was caused by the adhesion of ice to the moving parts or by solidification of the lubricant. The second type of failure was characterized by the failure of the breechblock slides to return to battery as the bolt closed. This type was apparently caused by the stiffness of the lubricant and lubricant-ice mixtures at low temperatures. Once the guns had been successfully charged with a live round and firing begun, stoppage due to a lubrication failure was very rare.

Two modifications in gun design were evaluated: oil-grooved breechblock slides and charger ram heads of reduced bearing area. The grooved slides improved the cold-sweat-cold test results by an average of one half cycle. However, the oil grooves upset the synchronization of the mechanism in ambient-temperature firing, impairing operation of the guns. The modified ram head appeared to offer little or no improvement.

Icing Resistance Tests

Cold-Sweat-Cold Piston and Cylinder Test — The development, construction, and use of the piston and cylinder device are described in Appendix A of Ref. 1 and in Appendix A of this report. The device consists basically of a cylinder containing a rotating piston lubricated with the grease being tested. The lubricated device was exposed to cold-sweat-cold conditions, and the torque necessary to rotate the piston within the cylinder was determined after each freezing.

In the present work, water was added into the apparatus after each sweat phase; this altered the nature of the results somewhat in comparison with those obtained previously when no water was added. When the same lubricants were tested by both methods, the revised method gave higher torques and roughly half as many cycles to failure as the original method. The rotating torques were more variable as a result of the wedging of ice sheets between the piston and the cylinder. The final rotating torque values, which previously were used as an indication of performance, could not be related to the gun firing test results.

When the breakaway torques (torque required to initiate rotation of the piston) for each cycle of the cold-sweat-cold piston and cylinder tests were plotted, the slopes of the curves were fairly reproducible although the individual points were somewhat scattered. Failure was taken as the point at which the smoothed curve exceeded 480 in.-oz. The correlation between the number of cycles to failure in the cold-sweat-cold piston and cylinder test and the number of cycles passed in the cold-sweat-cold gun firing test was poor. However, a fairly good correlation was found when only the frozen breechblock failures were considered. This relationship was to be expected, since failure in both cases was caused by ice adhesion following wash-off of the lubricant.

This correlation was weakened by the effect of variations in the room-temperature consistency of the lubricant on the piston and cylinder test. Among lubricants of the same composition, the ones surviving the greatest number of cycles were those having the highest apparent viscosities at room temperature. This was attributed to their greater resistance to wash-off during the sweating phases. Confirmation of this was later found in the cold-sweat-cold washing resistance test. On the gun, this advantage is offset by the adverse effects of high apparent viscosity at low temperatures.

The cold-sweat-cold piston and cylinder test is thus a useful screening test to detect lubricants of poor icing resistance. To be considered for gun testing, a lubricant should not fail before the tenth cycle. However, satisfactory performance does not necessarily predict satisfactory gun test performance.

Cold-Sweat-Cold Slider Test – The cold-sweat-cold slider test was devised in an effort to measure directly the shear strength of the bond formed by ice between two lubricated metal surfaces under cold-sweat-cold conditions. The test proved to be incapable of discriminating between various lubricants of similar and differing compositions. It was therefore of no use as a test of lubricant performance, but it was instructive in showing the effect of the metal surface on ice adhesion.

The ice adhesion was greater between rough steel surfaces than between smooth ones and was of intermediate strength between surfaces having the oil-retentive coating used on the gun parts. The gun might be made more resistant to icing by making susceptible parts smoother, thus reducing the "keying" of ice into surface irregularities.

Adhesion between the metal surfaces, particularly the rough ones, was reduced when thicker lubricant films were applied. A liberal coating of grease on the gun surfaces is necessary to insure that all depressions in the surface are filled; it also helps prevent the entrance of water between the sliding surfaces by forming a seal around them.

Water Resistance Tests

Fog Cabinet Test – In the original work on the semifluid lubricants, some reliance was placed on the observation of corrosion prevention and water resistance of lubricant films in the fog cabinet. This test was included in the specification (2). The present study revealed that fissuring and slumping of the grease film in the fog cabinet depended primarily on its thickness. Thin films (less than 0.020 in.) showed no effects, while thicker films (about 0.05 in.) were affected to various extents. The variations which were observed showed no correlation with the gun test performance, being mainly the consequences of variations in consistency.

As a corrosion test, the fog cabinet failed to cause rusting in any case, even with lubricant films as thin as 0.0025 in. The water drop washing resistance test was found to be a more severe corrosion test, capable of testing all lubricants to failure in a short time. The fog cabinet thus appears to have no usefulness as a screening test for gun lubricants.

Water Drop Washing Resistance Test – In this test, steel panels coated with grease were exposed to a continuous flow of salt water to determine the grease's relative resistance to washing and penetration of the rust-inhibiting film. This test showed no correlation with the gun tests or the piston and cylinder test. In the cold-sweat-cold tests, emulsion formation is the major cause of lubricant failure. In the water drop washing resistance test no emulsion is formed. The erosion of the grease film is caused primarily by the oil spreading onto the surface of the water drops, which were observed to be covered with a thin film of oil immediately after their formation. The rate of penetration of the bulk grease film in this test, therefore, does not have a great deal of relevance to the cold-sweat-cold tests.

The results of this test did appear to be useful in examining the lubricants' total effectiveness in preventing rusting of the lubricated surfaces. As in the fog cabinet test, both the physical barrier and the chemical inhibitor film had to be penetrated before rusting would occur. With its severity reduced by decreasing the concentration of the saline solution to 1% sodium chloride, this test was found to be suitable as a rust prevention test for use in specification of the lubricant.

Sustained Condensation Test – One of the best correlations with the gun tests was that of the rate of coalescence in the sustained condensation test, in which the behavior of moisture condensing on a grease-coated metal surface was observed. The greases most satisfactory in the gun tests permitted rapid coalescence of the moisture condensing on the grease film. With poorer greases a more stable emulsion was formed. The water droplets on the better greases were also more circular and showed larger contact angles. The visual observations do not yield quantitative data and would be influenced by the variation in experience and judgment of different observers. This makes the method undesirable for use as a standard test for specification.

The percentages of grease washed from the surface showed some regularities, but the method was not well suited to accurate determination of weight changes.

Cold-Sweat-Cold Washing Resistance Test – To investigate more fully the lubricant wash-off observed in the sustained condensation test, the cold-sweat-cold washing resistance test was developed. Here two factors in washing resistance were studied: the formation and melting of frost, and condensation. Thus, the conditions of the gun tests were more closely simulated. The use of thin metal panels permitted quantitative measurements of lubricant retention.

The most striking result from this test was the data on the amount of lubricant removed by the sweating process. With the 0.13-mm grease films used, one cold-sweat cycle typically removed one half of the lubricant. After four cycles, only 30% of the lubricant remained. The process appeared to remove the oil phase preferentially, leaving the remainder richer in solids and thus more viscous.

A strong correlation was found between the consistency of the lubricants tested and their resistance to wash-off. The higher the apparent viscosity, the more lubricant remained on the surface. Raising the apparent lubricant viscosity from 7000 cp to 40,000 cp doubled the retention. As previously noted, this effect influenced the results of the cold-sweat-cold piston and cylinder test, where greases of higher apparent viscosity passed more cycles before failure. Unfortunately, little correlation with the gun test was found. Although the effect undoubtedly was present, the small number of cycles and overshadowing by other factors made it insignificant.

Frost and Condensation Test – In order to study microscopically the effect on grease films of frost formation, condensation, and the subsequent refreezing of the collected moisture during cold-sweat-cold cycling, the frost and condensation test was devised. Although the conditions were not as carefully controlled as in the sustained condensation test, the same phenomena were observed and the apparatus was much simpler.

When the cold, grease-covered metal surfaces were exposed to moist air, microscopic ice crystals were seen to form in the air and fall onto the grease, where they were wetted by the oil present. Such projections then became preferred sites for further frost formation and grew upward as minute rods. Oil from the grease film spread up these rods, wetting the ice as it formed. Eventually the available oil became insufficient to wet the newly formed frost, and the frost from then on formed regular feathery crystals. No significant differences in the appearance of the frost on different lubricants was observed. As melting of the frost, moisture condensation, and coalescence were observed, differences were seen which were inter-related and also related to performance in other tests. The three most significant differences were:

1. the rapidity and extent of the retraction of the melted frost into discrete drops

2. the shape of the drops, whether circular and of high contact angle or irregular and of low contact angle

3. the amount of coalescing activity in the water-in-oil emulsion.

Arbitrary scores from 0 to 5 were assigned each observation, and the average of the nine scores from three cold-sweat cycles was determined.

These average scores correlated well with the cold-sweat-cold piston and cylinder test and the gun firing test, particularly the slides-out-of-battery failures. The best lubricants were those which showed rapid and extensive retraction of the water film from the melted frost, round drops of high contact angle, and active coalescence of water droplets in the water-in-oil emulsion. Apparently the poorer lubricants are covered with a more adherent water film after the sweating phase of the gun test and also contain more water in emulsified form. When the gun is chilled, there will be more ice to hinder its operation; and the grease containing emulsified water will become stiff when the water is frozen, because the ice then acts as an additional solid thickener.

The gun test performance of a lubricant can be roughly predicted by using the cold-sweat-cold piston and cylinder test to evaluate its ice adhesion resistance and using consistency data and the frost and condensation test to evaluate its resistance to stiffening at low temperatures. Unfortunately, the frost and condensation test is influenced by the experience and judgment of the observer. Thus, although it has been a very useful laboratory test method, it would not be suitable as a specification test procedure.

Emulsification Resistance Test – The important effect of emulsification on the performance of the lubricant has been demonstrated, but the previous techniques used to study emulsification and coalescence did not yield reproducible quantitative data. Examination of the thickener for surface-active impurities could forestall difficulties arising from this source, but this technique was not applicable to the finished lubricant. The emulsification resistance test, in which the diluted lubricant was emulsified with water and the rate of separation was observed, could detect such impurities in the finished lubricant, whether they were produced during manufacture or were present in any of the components. The procedure was simple and the results quantitative. Correlations with the frost and condensation test, the cold-sweat-cold piston and cylinder test, and the gun firing tests were good. The effect of the presence of surface-active material in the lithium stearate used in various lubricant samples was readily apparent.

CONCLUSIONS

1. The recent failures of the MIL-L-19701 semifluid aircraft machine gun lubricant in low-temperature firing tests were due to poor water resistance of the lubricant. It is probable that surface-active impurities such as myristate and oleate soaps in the lithium stearate thickener were responsible. Such impurities, particularly their sodium soaps, were found to reduce greatly the water resistance of these lubricants. Poor water resistance in greases of low consistency resulted in wash-off of the lubricant, followed by ice adhesion and frozen bolt failures. Poor water resistance in greases of higher consistency resulted in emulsification of water in the lubricant, followed by excessive stiffness at low temperatures and slides-out-of-battery failures.

2. A lubricant formulation including basic barium dinonylnaphthalene sulfonate as a rust inhibitor has been developed which offers improved performance. Samples of this lubricant have successfully passed the low-temperature firing test. The major advantages of the improved formulation lubricant are (a) less change in consistency over a wide range of temperatures, (b) improved water resistance, and (c) greater resistance to ice adhesion. None of the useful properties of the original formulation have been lost. The improvement in low-temperature consistency of the grease is large and is important to its good performance under the cold-sweat-cold test conditions. For lubricants of comparable room-temperature consistency, the apparent viscosity at -65 F of the improved lubricant is approximately 1 2 to 3 4 that of the original MIL-L-19701 lubricant. When first made, this grease typically has a low consistency. Structure build up occurs

with age and can be accelerated by heating. The optimum apparent viscosity is about 22,000 cp at 77 F, 30,000 cp at -65 F. Maximum and minimum consistency limits have been established. Revision of the specification to utilize this improved formulation is recommended.

3. A number of laboratory tests of icing resistance were evaluated, but none was found capable of replacing the cold-sweat-cold gun firing test. The cold-sweat-cold piston and cylinder test was found to be a useful test of ice adhesion resistance. Lubricants failing to pass ten cycles in this test are not likely to pass the firing test. It is recommended as a screening test for lubricants submitted by suppliers for qualification. Its use as an acceptance test is also recommended, as it is capable of detecting some deficiencies which might otherwise not be found.

4. An emulsification resistance test has been developed. The use of this test and the cold-sweat-cold piston and cylinder test will assure that the lubricant being purchased is satisfactory, once the supplier's product has been qualified by a firing test.

5. The relative amounts of harmful surface-active impurities in the soap can be determined by measuring the surface tension lowering resulting from their extraction from the thickener into water. A minimum purity standard can be established on the basis of a minimum surface tension for the thickener infusion.

6. The water resistance of other lithium stearate greases, both synthetic and petroleum-oil based, may also be adversely affected by surface-active impurities in the thickener.

7. For better lubrication and greater resistance to ice adhesion, the moving parts of the gun should be of smooth bare metal. Rough coatings should be applied only to exterior surfaces. Further mechanical modifications of the gun, such as oil-grooved slides, may be of some value, but should not be necessary if the lubricant quality is sustained.

ACKNOWLEDGMENTS

We are indebted to V. G. FitzSimmons of this Laboratory for many useful suggestions and observations, particularly during the gun firing tests, and for wear data. We are also indebted to W. D. Bascom of this Laboratory for development of the cold-sweat-cold slider test and for early work on the frost and condensation test. We wish to thank A. C. Samuels of the U.S. Naval Weapons Laboratory for the performance and evaluation of the gun testing. Acknowledgment is also made to the Lehigh Chemical Company, the General Electric Company, and the Dow Corning Corporation for supplying many lubricant and component samples.

REFERENCES

1. Baker, H.R., FitzSimmons, V.G., Singleterry, C.R., Sullivan, F.F., and Thomas, T.M., "The Development of a Rubber-Compatible and Ice-Resistant Lubricant for Aircraft Ordnance," NRL Report 4618, Oct. 28, 1955; NLGI Spokesman 20(No. 6):20 (1956)

2. Military Specification MIL-L-19701 (NOrd), "Lubricant, All-Weather, Semi-Fluid, for Aircraft Ordnance," Dec. 14, 1956

3. U.S. Naval Weapons Laboratory ltr WWE-1:ACS:jwg 8300 of Feb. 14, 1962

4. U.S. Naval Weapons Laboratory ltr WWE-1:ACS:mnm 8300 of Feb. 19, 1962

5. Baker, H.R., Bascom, W.D., and Singleterry, C.R., "The Adhesion of Ice to Lubricated Surfaces," NRL Report 5429, Feb. 9, 1960

6. U.S. Naval Weapons Laboratory ltr WWE-1:ACS:mcw 8300 of Sept. 26, 1962

APPENDIX A

EXPERIMENTAL PROCEDURES AND MATERIALS

PROCEDURES

Laboratory-Scale Grease Preparation

The preparation procedures for the improved lubricant are little different from those for the original material. The technique described is the "table top" method used for the preparation of laboratory samples.

For better oil retention, film stability, and water resistance in the finished grease, all of the components were combined before heating. The additives were dissolved in the esters with slight warming, and then the silicones were added. The lithium stearate was mixed thoroughly with the oil, care being taken to ensure that no dry lumps of the soap remained. Allowing the mixture to stand for an hour or two was found helpful in completing the wetting of the soap.

The mixture was heated to 200°C, where it was completely transparent, with no haze. The solution was then poured in a 1/8-in.-thick layer on a room-temperature soapstone slab to chill it. The grease was milled twice through a 3-in., three-roll paint mill, with the rolls set 0.0025 and 0.001 in. apart. It was then deaerated under vacuum and placed in an oven at 50°C to allow the consistency to build up for 8 to 32 hours.

Quick chilling of the hot solution was found to be important to the production of optimum grease structure. Some commercially prepared samples showed a coarse structure, grainy appearance, thixotropy, poor work stability, and dilatancy at some shearing rates. Similar properties were observed in laboratory samples which were chilled slowly or allowed to solidify at higher temperatures. More thorough milling was found to improve these greases by breaking down the coarse structure.

Gun Firing Tests

The gun firing tests with Mk 12 guns were conducted by the U.S. Naval Weapons Laboratory, Dahlgren, Virginia, in accordance with Par. 4.4.4.12 of Appendix B. Ungrooved breechblock slides were used in all test series except two, since these are presently in service. In most cases one new and one used gun and feeder were used to allow for variations in clearances caused by wear. The lubricants were applied liberally with a soft brush.

Cold-Sweat-Cold Piston and Cylinder Test

The apparatus and procedure used are described in Par. 4.4.4.11 of Appendix B. This procedure was changed somewhat from that described in Appendix A of Ref. A1. The addition of water after each sweating expedited the testing by increasing the severity and provided an excess of water for ice formation rather than the variable amount supplied by condensation alone. The stopper and cover were added to reduce the exposure of the lubricant to carbon dioxide when a chamber cooled by dry ice was used, and to

reduce the sublimation of ice from the apparatus. Exposure for 30 minutes in a low-temperature chamber with good air circulation was sufficient to cool the assembly to a temperature of -65 F, as measured with a thermocouple attached to the cylinder.

Cold-Sweat-Cold Slider Test

One end of a 3/4-in. cylindrical button or slider of metal was placed on a 1-in. square metal plate coated with the grease to be tested. The square plate rested on a block which could be cooled to about -80 F by circulating a refrigerant through it from a dry ice-acetone bath. Thawing and sweating were accomplished by bubbling air at 400 ml/minute through a saturated lithium chloride solution and passing it over the plate and slider. This low R.H. (15%) was used in order to adjust the severity of the test. The plate and slider were alternately frozen and sweated. After each sweating, the slider was slid back and forth once to allow some mixing of the water and grease. After each freezing the shearing force necessary to break the slider from the plate was measured using a lever and a small torque wrench.

The effect of the metal surface on adhesion was studied by substituting plates and sliders having similar geometry but different surface finishes. Polished stainless steel surfaces were prepared on a metallographic polishing wheel. Ground surfaces were prepared by grinding steel samples together with No. 220 silicon carbide. Samples of the finish used on the gun were obtained by cutting up parts from the gun.

Fog Cabinet Test

Steel panels coated with grease films 0.050 and 0.0025 in. thick were exposed to water fog in the fog cabinet (A2) for 24 hours to determine the rust inhibition and water resistance of the grease.

Water Drop Washing Resistance Test

The procedure used was that described in Par. 4.4.4.7 of Appendix B as a rust prevention test. A 3% sodium chloride solution was used in early work and a 1% solution in adapting the method for use in the specification.

Sustained Condensation Test

The sustained condensation test was devised to study the effect of water on thin films of grease on a metal surface. The metal surface, a stainless steel cylinder 3/4 in. in diameter and 1-1/2 in. long, was placed in a chamber in which the air was maintained at 26 °C and 93% R.H. Water from a constant-temperature bath at 19 °C was pumped through an axial passage in the cylinder to cool the surface below the dew point. In preparation for a test the surface was polished on a metallographic wheel, dried, and coated with a wedge-shaped grease film. The grease was applied with a glass rod touching the surface at one end and spaced 0.02 mm (0.0008 in.) from the surface at the other end with a Teflon film.

The condensation of water on the grease film was observed with a microscope to detect differences in the behavior of the various lubricants. The percentage of grease removed from the surface was determined by weighing the metal cylinder before and after the test.

Cold-Sweat-Cold Washing Resistance Test

Steel panels were prepared and coated with the lubricant exactly as for the water drop washing resistance test. Each panel was weighed before and after being coated with the lubricant. The panel was laid on a 1-in.-thick steel block heat sink with a few drops of water between panel and block to improve thermal contact, and the assembly was placed in a chamber cooled to -65°F by dry ice. After one hour the panel and steel block were placed 30° from horizontal in the same room-temperature humidity chamber used for the cold-sweat-cold piston and cylinder test. The average relative humidity was 81%. After the frost formation, melting, and run-off were observed (about 20 minutes), the panel was dried, weighed, and again placed in the cold chamber on the steel block. Four such cycles were made and the percentage of lubricant remaining on the panel after each cycle was computed.

Frost and Condensation Test

The metal surface used was the polished end of a 3/4-in. stainless steel button, identical to that used as a slider in the plate and slider test. It was cleaned by wiping and washing with acetone and benzene, or if a lubricant having a different rust inhibitor was to be tested, by repolishing. A wedged grease film was applied, being about 0.1 mm at its thickest point. Exact control of thickness and uniformity was not required.

The button was cooled to -65°F, then placed in air at ambient temperature and 40 to 65% relative humidity. A 30X binocular microscope was used to observe the frost formation, melting, and condensation. Each sample was observed for three cold-sweat cycles. Arbitrary numerical scores were assigned for various observed variations, such as rapidity of retraction of the water film after melting, irregularity of the water droplet shapes, activity of coalescence, and the amount of oil-in-water emulsion formed.

Surface Tension Measurements

The lithium stearate infusions were prepared as described in Par. 6.4 of Appendix B. The surface tensions were determined at 25°C by the ring method using a du Nouy tensiometer and employing the corrections of Harkins and Jordan (A3).

Emulsification Resistance Test

The procedure followed in the emulsification resistance test is described in Par. 4.4.4.10 of Appendix B.

Measurements of Consistency

In this study, only apparent viscosity measurements were used to examine the grease consistencies. The techniques used are described in Par. 4.4.4.2 of Appendix B. Both the LVF model (four speed) and LVT model (eight speed) Brookfield viscometers used were well within the maximum permissible error of 1% of full scale when checked against a Brookfield viscosity standard of 30,300 cp.

Most measurements of consistency at -65°F were made in a small chamber cooled by circulating alcohol. The coolant was circulated through a coil in a dry ice-acetone bath and around the chamber by a thermostatically controlled pump. The beaker containing the grease sample was inserted in an aluminum heat sink, and the temperature of the grease was determined with an immersed thermocouple. The viscometer spindle, without

extension shaft, passed through the cover of the chamber. The use of containers 3 cm rather than 4.5 cm in diameter as previously required introduced no error. In fact, placing the spindle 1 cm from the wall of the container caused no appreciable error in the measurement.

The apparent viscosity-temperature profiles for a number of greases were determined. The apparent viscosity was measured at a number of temperatures from 170 to -90 F. The lubricant sample was in a controlled-temperature chamber, and an extension shaft was used with the viscometer. Before measurements which were made above room temperature, the samples were stirred to prevent errors due to oil bleeding around the viscometer spindle.

The effect of aging on lubricant consistency was studied by making frequent measurements of the apparent viscosities of samples stored at constant temperatures. Samples were kept at 25 °C in a constant-temperature room, and at 50 and 65 °C in thermostatically controlled ovens. The samples were brought to 25 °C before measurements were made. These samples were also used to determine the effect of aging on apparent viscosity-temperature characteristics and cold-sweat-cold piston and cylinder test performance.

Four-Ball Wear Test

To ensure that the wear characteristics of new grease formulations would be satisfactory, oil blends were made up and tested on the four-ball wear machine. The equipment and experimental technique have been previously described (A4). The tests were made with a 20-kg load at 140 °F, the machine running at 700 rpm for two hours.

Iodine Value

Lithium stearate samples were hydrolyzed in dilute sulfuric acid, and the fatty acids extracted with ether, washed with saturated sodium chloride solution, and dried.

The iodine values of the fatty acid samples were determined by the Wijs method (A5).

Chromatographic Analyses of Acids

The fatty acid samples, as prepared for the iodine value determinations, were analyzed by liquid-liquid column chromatography using the method of Howard and Martin (A6). Paraffin oil on hydrophobic silica was used as the stationary phase and aqueous acetone as the moving phase. The separation was followed by titrating the eluate with 0.01N methanolic potassium hydroxide. For the determination of stearic, palmitic, and oleic acids, 4-mg samples were developed with 65% aqueous acetone. For the determination of myristic acid, 80-mg samples were dissolved in acetone which was then diluted with water to 60% acetone. The stearic and palmitic acids which came out of solution were filtered off, and the filtrate was loaded into the column and developed with 60% aqueous acetone.

The residues from lithium stearate infusions were also analyzed. As these residues were available in only milligram amounts, they were hydrolyzed in the loading solvent. This solvent was 60% acetone and 40% 0.03N sulfuric acid. The developing solution was 60% aqueous acetone. In the eluate the fatty acids were separated from the sulfuric acid well enough to permit quantitative determinations.

Spectrographic Analyses of Soaps

Analyses of the metals present in several soap samples were made by emission spectrography. To detect the presence of sodium, the flame test was sufficiently sensitive.

Flash Point

Oil flash points were determined using the Pensky-Martens closed tester according to ASTM Method D93-62 (A7).

MATERIALS

Oils

1. Bis(2-ethylhexyl) sebacate was supplied by Rohm and Haas as Plexol 201. It was used as received and also after purification by distillation and percolation over adsorbents.

2. Isodecyl pelargonate was supplied by Emery Industries as lubricant ester 963.

3. Dimethyl silicone fluid, 7 cs, was supplied by the Dow Corning Corporation as DC 200, 7.5 cs; by the General Electric Company as SF-96, 7.5 cs; and by the Union Carbide Corporation.

4. The slightly phenylated silicone fluid, 50 cs, was supplied by the Dow Corning Corporation as DC 510, 50 cs, and by the General Electric Company as SF-81, 50 cs.

Additives

1. Phenylstearic acid was obtained from various sources, including Barlow Chemical Corporation.

2. Basic barium dinonylnaphthalene sulfonate (symbol Ba(DNNS)OH) was supplied by the R.T. Vanderbilt Company as 50.5% solution in heptane, base No.: 50, designated No. 83-123.

3. Neutral barium dinonylnaphthalene sulfonate was supplied by the R.T. Vanderbilt Company as a solution in low-boiling naphtha, designated Na-Sul 72-80-B.

4. Myristic acid was U.S.P. grade.

5. Oleic acid was U.S.P. grade.

6. Sodium dinonylnaphthalene sulfonate was supplied by King Organic Chemicals, Inc., as a 51% solution in naphtha, designated No. 85-49.

7. Ethylenediamine dinonylnaphthalene sulfonate was supplied by King Organic Chemicals, Inc., as a 52% solution in naphtha, designated No. 85-47.

8. 4-tert-Butyl-2-phenylphenol was obtained from the Dow Chemical Company.

9. Phenyl-α-naphthylamine was obtained from Eastman Organic Chemicals and E.I. du Pont de Nemours and Company, Inc.

10. 2,6-Di-tert-butyl-4-methylphenol is available as Parabar 441 from the Enjay Chemical Co.

Thickeners

1. Lithium stearate was obtained from the lubricant manufacturers, the Witco Chemical Company, Inc. (products No. 306 and 304), and Foote Mineral Company (Litholite W, lot 701-1).

2. Lithium oleate and myristate were prepared by slowly adding an excess of the acid to aqueous lithium hydroxide while stirring. (The myristic acid was in acetone solution.) The soap was filtered off, washed with water followed by acetone, and dried.

REFERENCES

A1. Baker, H.R., FitzSimmons, V.G., Singleterry, C.R., Sullivan, I.F., and Thomas, T.M., "The Development of a Rubber-Compatible and Ice-Resistant Lubricant for Aircraft Ordnance," NRL Report 4618, Oct. 28, 1955

A2. Federal Test Method Standard No. 791, Method 5312.1

A3. Harkins, W.D., and Jordan, H.F., J. Am. Chem. Soc. 52:1751 (1930)

A4. Clinton, W.C., "A Study of the Four-Ball Wear Machine," NRL Report 3709, Sept. 1950

A5. "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Washington, D.C.: A.O.A.C., p. 430, 1940

A6. Howard, G.A., and Martin, A.J.P., Biochem. J. (London) 46: 532 (1950)

A7. "1964 Book of ASTM Standards, Part 17," Philadelphia: American Society for Testing and Materials, 1964

APPENDIX B

RECOMMENDED TECHNICAL REQUIREMENTS FOR REVISION OF SPECIFICATION MIL-L-19701 (NOrd)

1. SCOPE

1.1 This specification covers a semifluid lubricant intended for the lubrication of aircraft machine guns and accessory equipment between -65 and 160 F and under cold-sweat-cold cycling conditions. It is required to be compatible with oil-resistant rubber covered by specification MIL-P-5516.

2. APPLICABLE DOCUMENTS

2.1 The following specifications and standards of the issue in effect on the date of invitation for bids form a part of this specification:

Military specifications

MIL-P-5516 - Packings and Gaskets, Hydraulic, Aircraft.

ASTM standards

Book of ASTM Standards - 1964, Part 17
Book of ASTM Standards - 1964, Part 18
Book of ASTM Standards - 1961, Part 11.

3. REQUIREMENTS

3.1 Qualification – The synthetic lubricant furnished under this specification shall be a product which has been tested and has passed the qualification tests specified in 4.4.1.

3.2 Composition – The lubricant shall be of an approved composition consisting of components of a grade and quality which have been demonstrated under firing tests to be suitable for the purpose intended and which will formulate a semifluid lubricant that conforms to all of the requirements of this specification (See 6.3).

3.3 Consistency –

3.3.1 Apparent Viscosity – The apparent viscosity of the lubricant shall be measured in accordance with 4.4.4.2. Measurements shall be made on the lubricant as received, on a sample after storage for 168 hours at 77 F, and on a sample after storage for 168 hours at 120 F. All three consistencies shall be within the following limits:

a. At 77 F, maximum of 30,000 cp, minimum of 16,000 cp.

b. At -65 F, maximum of 40,000 cp.

c. Maximum difference of 20,000 cp between -65 F and 77 F apparent viscosities.

3.3.2 Work Stability – The apparent viscosity after working in accordance with 4.4.4.3 shall not be less than 91% of the original apparent viscosity.

3.4 Evaporation – The evaporation loss when determined in accordance with 4.4.4.4 shall fall between 12 and 24% in 20 hours and shall not exceed 50% in 100 hours.

3.5 Storage Stability – The lubricant shall show no gross separation of oil and soap phases under the conditions of 4.4.4.5. The accumulation of a thin film (less than 1 mm) of oil at the upper surface of the material or at the bottom of the sample bottle shall not be cause for rejection.

3.6 Oxidation Stability – The Oxygen pressure drop, when tested in accordance with 4.4.4.6 at 210°F, shall not exceed 5 psi in 100 hours.

3.7 Rust Prevention – The lubricant shall inhibit rusting of the surface of steel test panels prepared and exposed according to 4.4.4.7. At least three out of the four exposed panels shall be free of any trace of rust.

3.8 Rubber Compatibility – The lubricant shall not cause a change in weight of O-rings fabricated from MIL-P-5516 rubber which differs by more than 3% from that produced in O-rings of the same lot by the reference fluid. The method of test is specified in 4.4.4.8.

3.9 Workmanship – The component materials shall be thoroughly mixed to form a uniform product free of dirt, grit, water, or other foreign materials. When examined as specified in 4.4.4.9, the test panel shall emerge from the bulk lubricant with a uniform translucent coating, showing no evidence of lumps or nonhomogeneous structure.

3.10 Emulsification Resistance – The lubricant shall be diluted and emulsified with water in accordance with 4.4.4.10. When examined after standing for 30 minutes, at least 5 ml of water shall have separated from the emulsion to form a continuous water layer.

3.11 Icing Resistance – The sample lubricant shall be tested three times in accordance with 4.4.4.11, each test consisting of 15 sweat-cold cycles. Encountering breakaway torques of greater than 480 in.-oz in more than 5 of the 45 cycles shall constitute failure.

3.12 Machine Gun Performance Test – The lubricant shall permit satisfactory performance of a Mk 12 20-mm machine gun equipped with a Mk 7 pneumatic feeder when tested by the method described in 4.4.4.12.

4. QUALITY ASSURANCE PROVISIONS AND TEST PROCEDURES

4.1 Lot –

4.2 Sampling –

4.2.1 Qualification Test Sample – The qualification test sample shall consist of 5 lb of lubricant. A sample of each constituent material shall also be furnished: 1 pint of each of the oils, 2 oz of the thickener, and 1 oz of each of the additives, all drawn from the materials used in actual production of the lubricant sample submitted. The manufacturer shall supply the Government testing activity and the Bureau of Weapons with certified statements of prior tests showing that the sample being submitted conforms with all the requirements of this specification, except for machine gun performance tests. Qualification samples shall be accompanied by a certified statement giving the complete formula for the lubricant submitted and the chemical composition and source of materials used therein. All information furnished will be held in commercial confidence. Approval granted on a lubricant shall not apply if any of the components have been changed in type, grade, or quantity.

4.2.2 Confirmation Test Sample – The confirmation test sample shall be taken from the first batch of lubricant offered for delivery on a contract or order after the lubricant has passed the qualification tests. Samples shall otherwise be as specified in 4.2.1.

4.2.3 Sampling for Lot Acceptance Tests – The Government inspector shall select a sample of not less than 3 lb of lubricant from each lot submitted for acceptance under a contract or order in accordance with the procedure outlined in ASTM Method D270-61, Book of ASTM Standards - 1964, Part 18.

4.2.4 Sampling for Inspection of Containers –

4.3 Inspection –

4.3.1 Inspection –

4.3.2 Inspection of Containers –

4.3.3 Contractors Inspection –

4.4 Tests –

4.4.1 Qualification Tests – Tests for qualification shall consist of all the tests of this specification, including firing tests as specified. Failure of a qualification sample to comply with any of the test requirements of this specification shall result in the withholding of qualification.

4.4.2 Confirmation Tests – Tests for confirmation shall consist of all of the tests of this specification, including firing tests as specified. If the qualification test sample is taken from a production batch, no confirmation testing shall be required.

4.4.3 Lot Acceptance Tests – Tests for lot acceptance shall consist of all the tests of this specification except firing tests. The right is reserved to make any additional tests deemed necessary to determine that the lubricant meets the requirements of the specification. Lots shall be accepted or rejected by the Government inspector on the basis of the laboratory test report on the transmitted samples. Failure of a sample to comply with any of the acceptance test requirements shall result in the rejection of the lot represented. Rejected lots may be resubmitted for acceptance tests, provided that the contractor has removed (or reworked) all nonconforming products.

4.4.4 Test Methods –

4.4.4.1 Composition – The composition of the lubricant shall be certified by the manufacturer at the time of delivery.

4.4.4.2 Apparent Viscosity – The apparent viscosity shall be measured with a Brookfield model LVF or LVT viscometer under the following conditions. The immersed portion of the rotating spindle shall be a cylinder 3.1 cm long and 0.32 cm in diameter (No. 4 spindle immersed to center of immersion groove). The grease shall be contained in a beaker or cylinder not less than 3.0 cm in diameter to a depth of not less than 4.5 cm. All measurements shall be made with the rotor guard removed from the instrument, and apparent viscosity shall be computed without the application of the correction factors normally applied when the instrument is used without a guard. Grease samples shall be stirred to ensure uniformity but shall not be worked (except as required for 3.3.2). The temperature of the lubricant shall be checked before measurements by immersing a thermocouple or thermometer in the lubricant to ensure that the temperature is at 77 ± 1 or -65 ± 2 F. When measuring the apparent viscosity at -65 F, the sample shall be held undisturbed at -65 F, with the spindle immersed, for two hours before beginning

measurements. The instrument shall be used with an extension shaft if necessary, so that the instrument proper remains outside the cold chamber.

The spindle shall be rotated in the lubricant at 60 rpm for at least one minute, after which readings shall be made at 60, 30, 12, and 6 rpm followed immediately by a series at 6, 12, 30, and 60 rpm. The spindle shall be allowed to rotate at each speed until a constant reading is obtained. Pairs of readings at the same speed should not differ by more than 10%. The value of apparent viscosity reported shall be that computed from the average of the two readings at 12 rpm.

4.4.4.3 Work Stability – The apparent viscosity of a portion of the lubricant sample shall be determined at 77 ± 1 F in accordance with 4.4.4.2. This portion shall then be worked an amount equivalent to ten passes through a 100-mesh screen in the NRL microworker (see 6.5). The apparent viscosity of the worked lubricant shall be determined, again at 77 ± 1 F in accordance with 4.4.4.2, and the change in apparent viscosity calculated.

4.4.4.4 Evaporation – Evaporation characteristics of this lubricant shall be determined by the methods and with the equipment of ASTM test method D972-56 for the evaporation losses of oils and greases, using the evaporation cell for oils, and a test temperature of 210 F. The weight of sample taken for test shall be 1.00 g evenly distributed over the bottom of the test cell. The weight lost by evaporation shall be measured after 20 hours and after 100 hours at the test temperature.

4.4.4.5 Storage Stability – The contents of the original container of synthetic lubricant taken for sampling shall be thoroughly mixed by stirring and a 75-ml sample then transferred to a 4-oz cylindrical oil sample bottle having an outside diameter of 1-1 2 ± 1 16 in. After shaking, bottle and sample shall then be stored without further disturbance in an oven at 120 F for a period of one week and then examined for evidences of oil separation.

4.4.4.6 Oxidation Stability -- The oxidation stability of the lubricant shall be determined in accordance with ASTM test method D942-50.

4.4.4.7 Rust Prevention – Steel panels, SAE 1010 or 1020, 3 × 6 × 1 32 in., shall be prepared as follows: (a) remove obvious contamination, rust, preservatives, etc., (b) wash with hot water and detergent, (c) rinse thoroughly with hot water, (d) rinse with acetone, (e) polish with clean, grade 1 emery paper, (f) rinse with hot tap water followed by distilled water, and (g) allow to dry. The lubricant shall immediately be applied with a glass rod, worked into the surface, and the excess struck off with the rod spaced 0.005 in. above the surface (two layers of cellophane tape) to leave an even film of the lubricant of approximately this thickness. The panel shall be placed with one end elevated so that the panel is inclined 15 from the horizontal. A glass buret tip or other small glass tube shall be mounted vertically above the panel with the end of the tube 1 32 to 1 16 in. above the lubricant film. The tube shall be located equidistant from the sides of the panel and 1 to 2 in. from the upper end. A 1 solution of pure sodium chloride in distilled water shall be allowed to run from the tube onto the lubricant film at 3 0.2 ml minute. Constant flow rate can be achieved by siphoning the solution from a constant-level reservoir. After 100 ml of the solution have passed over the panel, it shall be examined for evidence of rusting. Four such tests shall be made on the lubricant sample.

4.4.4.8 Rubber Compatibility – The change in weight shall be determined by the general procedure of section 8 of ASTM Method 471-59T, ASTM Standards - 1961, Part 11, with the following specific provisions:

a. The test pieces shall be rubber O-rings of approximately 1.3 cm external diameter, and having a cross-sectional diameter of approximately 0.17 cm. (An example of

an O-ring meeting the requirements is that specified in Air Force-Navy Aeronautical Standard Drawing AN 6227B-7, referred to in specification MIL-P-5516.) They shall be fabricated from rubber meeting the requirements of MIL-P-5516.

b. The test temperature shall be 160 F.

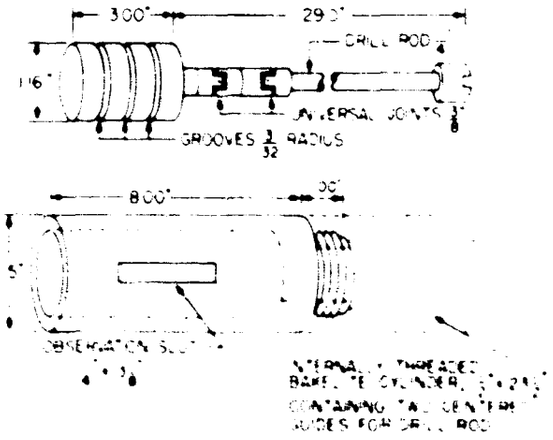
c. The change in weight of the test specimens shall be determined after 72 hours of contact with the lubricant.

d. The weight gain produced by the lubricant under examination shall be compared with that produced in O-rings of the same lot by a reference fluid containing 65 wt-% of a silicone fluid corresponding to component d and 35 wt-% of component b of Table B1.

4.4.4.9 Workmanship – A smooth steel panel, 2 × 4 in., shall be dipped in the vertical position into the recently agitated lubricant. This panel is then removed with a smooth vertical motion and examined for lumps, inhomogeneities, and foreign matter.

4.4.4.10 Emulsification Resistance – 5 ± 0.1 ml of the lubricant shall be placed in a 50-ml graduated cylinder, of 16 to 20 cm internal height, having a ground-glass stopper. To this shall be added 25 ± 0.2 ml of heptane, at least 96% pure, and the lubricant mixed with the heptane by shaking. Then 20 ± 0.2 ml of distilled water shall be added, and the cylinder shall be shaken vigorously by hand for 30 seconds. The mixture shall then be allowed to settle undisturbed at room temperature for 30 minutes ± 30 seconds.

4.4.4.11 Icing Resistance – The apparatus shall consist of a steel cylinder containing a movable steel piston as specified in Fig. B1, a rubber stopper to fit the end of the cylinder, and an observation slot cover of sheet metal rolled to fit the outside of the cylinder. Torque wrenches covering the range from 0 to 480 in.-oz shall be used to measure the torque required to rotate the piston. A mechanical or dry-ice refrigerator shall be arranged so that the cylinder is exposed to circulating air (or carbon dioxide) at about -70 F while the other end of the device is accessible for making torque measurements. A sweat box of not less than 1000 cu in. volume shall be arranged to expose the piston and cylinder to circulating air at room temperature and between 75 and 85% relative humidity.



The piston and cylinder shall be cleaned by washing alternately with C.P. benzene and acetone. Five ml of the lubricant are then applied to the piston from a syringe. The piston is rotated until it is covered with the lubricant and the grooves are full. The remainder of the lubricant is left in the observation slot. The end of the cylinder is stoppered and the slot cover placed on the cylinder. The device shall then be inserted into the cold chamber in a horizontal position with the observation slot uppermost, and the piston centered on the slot. When the device has cooled to -65 ± 2 F (30 to 60 minutes), sweat-cold cycling shall be conducted as follows. The device is removed from the cold chamber and inserted in the sweat box with the stopper and cover removed and the piston pushed out of

the cylinder so that 7/8 of its length is exposed. After 30 minutes, the piston shall be repositioned in the cylinder, the exterior surface of the cylinder wiped free of water, and the stopper placed in the end of the cylinder. One ml of distilled water is poured into the observation slot, and the piston is rotated to distribute the water. The slot cover is replaced, and the device is inserted into the cold chamber as before. When the device has cooled to -65 ± 2 F, the torque necessary to initiate rotation of the piston within the cylinder (breakaway torque) shall be measured by applying a torque wrench to the exposed end of the rod. The piston shall then be rotated through two revolutions if this can be done without excessive force. When it is necessary to interrupt the cycling, the device shall be left in the cold chamber. Preferably, interruptions should be scheduled at the end of a cycle, after measurement.

4.4.4.12 Machine Gun Performance Test – The lubricant must provide acceptable performance as the sole lubricant on the entire Mk 12 20-mm gun and on the pneumatically operated Mk 7 ammunition feeder. The lubricant performance shall be determined with two basic machine gun assemblies. The guns and feeders shall be completely disassembled, and all elastomeric seals shall be removed and discarded. The gun and feeder components shall be cleaned of all traces of lubricant by washing in a volatile solvent such as Stoddard solvent, Varsol, or unleaded gasoline. No chlorinated solvents shall be used. After all solvent has been removed, all surfaces of the gun and feeder components shall be liberally coated with the lubricant, applied with a soft-bristled brush or by wiping it on with a saturated lint-free cloth. All elastomeric seals shall be installed after the surfaces have been covered with lubricant. These seals must conform to Specification MIL-P-5516 and shall be new and free from flash and blemishes. The gun and feeder shall then be reassembled and test fired at normal ambient temperature. This firing shall consist of four 100-round bursts with the gun permitted to cool between bursts. The rate of fire of the last burst shall at least equal the acceptance rate for the Mk 12 gun. The guns and feeders shall then be disassembled, cleaned, and relubricated; and new elastomeric seals shall be installed during reassembly.

The ammunition to be used shall be lubricated with the same lubricant used on the guns. Lubricated dummy rounds shall be inserted in the chambers and the bolts closed. The guns, feeders, and ammunition shall then be chilled at -65 F for 90 minutes, exposed to 60 ± 3% relative humidity and 60 F temperature for 90 minutes, and then chilled at -65 F temperature for 90 minutes, after which each gun shall be charged and a 50-round burst shall be fired. Failure of either gun to charge, feed, or fire during four consecutive cold-sweat-cold cycles shall be cause for disqualification of the lubricant. No cleaning or relubrication shall be done during the four cold-sweat-cold cycles. The rate of fire shall not drop more than 150 rounds/minute below the average rate of fire established at normal ambient temperatures on the same gun. To fire the gun it shall be charged solely by the pneumatic system; no manual assistance to the charger or feeder is permitted. Upon each removal from the sweating cabinet, the guns shall be allowed to drain briefly with the muzzles elevated. During overnight interruptions, the guns, feeders, and ammunition for the next bursts shall be kept at -65 F.

The mechanical failure of any gun or feeder part shall not be cause for repetition of the test provided 25 rounds have been fired at an acceptable rate. The gun or feeder may be disassembled and replacement parts installed, with only the replacement parts receiving lubricant. Only one such disassembly shall be permitted during the required four cold-sweat-cold cycles; the need for further disassembly shall cause the test to be discontinued and a new test started. The facility conducting the tests shall provide satisfactory moisture- and oil-free air through air lines delivering satisfactory volume and pressure.

5. PREPARATION FOR DELIVERY

5.1 Application –

5.2 Packaging –

5.3 Packing –

5.4 Marking – Suggested label information: "This lubricant is compatible with MIL-P-5516 oil-resistant rubber. CAUTION: Contains a silicone component which can cause temporary irritation of the eyes. Avoid transfer of grease from hands to skin near the eyes. Store in a cool place. Shake before using."

6. NOTES

6.1 The synthetic lubricant covered by this specification is intended for use on the entire assembly of aircraft machine guns, associated mechanisms, and other weapons or equipment to ensure their functioning at low temperatures and under icing conditions.

6.2 Ordering Data –

6.3 A lubricant which has been found to comply with all the requirements of this specification has the formulation shown in Table B1. Any other formulations or compositions must be demonstrated to be satisfactory for the purpose intended.

Table B1
Lubricant Composition

Component	Weight-%	
a. Isodecyl pelargonate, lubricant grade*	28.6	± 0.5
b. Bis(2-ethylhexyl) sebacate, lubricant grade†	9.0	± 0.5
c. Dimethyl silicone fluid, 7 cs‡	39.2	± 1.0
d. Slightly phenylated silicone fluid, 50 cs§	14.2	± 0.5
e. Phenylstearic acid	1.0	± 0.05
f. Basic barium dinonylnaphthalene sulfonate (50% in volatile solvent)¶	2.0	± 0.1
g. Oxidation inhibitor**	0.4	± 0.05
h. Lithium stearate††	5.6	± 1.5

*Equivalent to that supplied by Emery Industries as Lubricant Ester 963.
†Equivalent to that supplied by Rohm and Haas as Plexol 201.
‡Equivalent to that supplied by Dow Corning Corporation as DC-200, 7.5 cs.
§Equivalent to that supplied by Dow Corning Corporation as DC-510, 50 cs.
¶Equivalent to that supplied by R. T. Vanderbilt Co., Inc.
**4-tert-butyl-2-phenylphenol, phenyl-α-naphthylamine, and 2,6-di-tert-butyl-4-methylphenol have been found satisfactory.
††See 6.4.

6.4 The use of a very pure grade of lithium stearate is essential to attain the required performance by the finished lubricant. The following procedure may be used to determine the suitability of the lithium stearate for this use. An infusion of the lithium stearate shall be prepared by briefly boiling 0.75 g of the lithium stearate in 25 ml distilled water and filtering through fine filter paper. Care shall be taken to exclude detergents and other surface-active materials. The infusion shall not be diluted or allowed to evaporate appreciably. The surface tension of the infusion shall then be measured by the ring method. ASTM test method D971-50 shall be followed in regard to the apparatus, the preparation of the apparatus, and the calibration of the apparatus. The procedure used is that described in this test method for the determination of the surface tension of water (paragraphs 7.(a) and (b)). That portion of the procedure dealing with oil-water interfacial tension is not used. The surface tension of the infusion should be no less than 38 dynes cm.

6.5 The Naval Research Laboratory microworker is described in an article by G.M. Hain, ASTM Bulletin 147, p. 86 (August 1947).

6.6 Qualification –

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a REPORT SECURITY CLASSIFICATION
U.S. Naval Research Laboratory Washington, D. C. 20390	UNCLASSIFIED
	2b GROUP

3 REPORT TITLE

FACTORS AFFECTING THE ICING RESISTANCE OF LUBRICANTS FOR AIRCRAFT ORDNANCE

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

A final report on one phase of the problem.

5 AUTHOR(S) *(Last name, first name, initial)*

Baker, H.R., and Bolster, R.N.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
October 21, 1965	38	13

8a CONTRACT OR GRANT NO.	9a ORIGINATOR'S REPORT NUMBER(S)
NRL Problems C02-04 and C02-12 b. PROJECT NO. RRMA03-021/652-1/R001-07-01-17-3 RR 001-01-43-4752 d.	NRL Report 6329 9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10 AVAILABILITY/LIMITATION NOTICES

Distribution of this document is unlimited.

Available at CFSTI.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Dept. of the Navy (Bureau of Naval Weapons and Office of Naval Research)

13 ABSTRACT

Recent samples of the all-weather semifluid lubricant for aircraft ordnance, both from manufacturers and from Navy stocks, have failed to meet the cold-sweat-cold gun firing test required by Military Specification MIL-L-19701 (NOrd). These failures were due to ice adhesion attendant on the poor water resistance of the lubricants. The probable cause of the loss in water resistance was the presence in the lithium stearate thickener of surface-active impurities such as sodium soaps and soaps of myristic and oleic acids. These impurities can be detected by measurements of surface tension lowering. It is probable that the water resistance of other lithium stearate thickened greases are also affected by these impurities. The investigation established that variations in raw materials other than the soap were not major contributors to the difficulties encountered.

A lubricant of altered formulation has been developed and shown to be superior to the original lubricant. Variations in the consistency of the improved lubricant over a wide temperature range were found to be much less than those of the original lubricant. Resistance to water and to ice adhesion are increased. This material has successfully lubricated the Mk 12 machine gun equipped with the Mk 7 pneumatic feeder under ambient temperature and cold-sweat-cold conditions. This formulation retains all of the useful properties of the original lubricant, such as compatibility with MIL-P-5516 oil-resistant rubber, resistance to evaporation loss, corrosion inhibition, and antiwear protection.

Several new testing procedures have been developed and evaluated, and existing tests have been re-examined. No reliable substitute for the gun firing test has been found, but screening tests for evaluating separately some of the lubricant's qualities have been developed and norms established for greases known to be successful in the gun firing tests.

DD FORM 1 JAN 64 1473

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lubricants						
Aircraft machine guns						
Gun testing						
Icing resistance						
Rust inhibiting						
Water resistance						
Thickeners						
Oils						
Greases						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.